



Consommation
et Corporations Canada

Consumer and
Corporate Affairs Canada

Bureau des brevets

Patent Office

Ottawa, Canada
K1A 0C9

(21) (A1)	2,023,691
(22)	1990/08/21
(43)	1991/02/24
(52)	18-29

5,034,5/21

(51) INTL.CL. ⁵ C08J-9/28; B01D-61/36; B01D-53/22; B01D-71/26

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Composite Membrane, Its Use and Processes for
Pervaporation and Gas Separation Using This Composite
Membrane

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(30) (DE) P 39 27 787.9 1989/08/23

(57) 9 Claims

Notice: The specification contained herein as filed

Canada

CCA 3254 (10/89) 41

Composite membrane, its use and processes for pervaporation and gas separation using this composite membrane

A b s t r a c t

A composite membrane consisting of

- i) a microporous membrane, containing inorganic fillers, of a film-forming thermoplastic polymer, the fillers having a specific surface area of 5-200 m²/g and representing 60-90% by weight of the total weight of the membrane, and
 - ii) a permselective elastomeric separating layer applied to the membrane,
- is excellently suitable for processes for pervaporation and gas separation.

The invention relates to new composite membranes, a process for their preparation and processes for pervaporation and gas separation using these composite membranes.

5 In pervaporation, a mixture of different liquid substances in liquid or vaporized form (feed) is brought up to a membrane which has different permeabilities to the individual substances of the feed. On the other side of the membrane, a gaseous permeate which is highly
10 enriched or depleted in individual substances or groups of substances of the feed is collected. This permeate can be condensed again, for example for further processing. If the feed is composed of a mixture of gaseous substances and if the driving force of the membrane process is
15 essentially produced by application of an increased pressure on the feed side, this process is to be equated technologically to gas separation.

Pervaporation processes are useful additions to other processes of substance separation, such as distillation or absorption. They provide a useful service, for
20 example, in the separation of substance mixtures which boil azeotropically and in the removal of low concentrations of undesirable substances in ecologically relevant separation tasks.

25 Various materials have been employed to date for the production of permselective membranes, that is to say non-porous plastic membranes of polyethylene (US 2,953,520) and polyurethane membranes (US 3,776,970

and DE-AS 2,627,629).

The following requirements, inter alia, are to be met for economic use of pervaporation membranes:

- 5 (a) the highest possible selectivity in respect of the substances to be separated,
- (b) the highest possible permeation stream density and
- (c) the longest possible life (mechanical and chemical stability).

10 The properties required are often excluded from the property profile of conceivable materials, so that many film-forming polymers are excluded from use in membrane technology. A particular problem is the realization of a high permeation stream density. In principle, the thinnest possible membrane having a selective action
15 is required for this, but this in turn generally does not have the required mechanical stability. Composite membranes which consist of a porous support structure and a thin layer having a selective action have therefore already been proposed (Chem.-Ing.-Tech. 60 (1988), 590).
20 Ultrafiltration membranes are proposed in this context for the porous support structure, but their surface porosity, because of their intended use, is very low so that a certain permeation stream density cannot be exceeded.

25 It has now been found that the ultrafiltration membranes known from EP 77,509, together with a perm-selective elastomeric separating layer, give composite membranes which combine a high selectivity with high permeation stream densities and excellent chemical and
30 mechanical resistance.

The invention accordingly relates to composite membranes consisting of

- i) a microporous membrane, containing inorganic fillers, of a film-forming thermoplastic polymer, the fillers having a specific surface area of 5-200 m²/g and representing 60-90% by weight of the total weight of the membrane, and
- ii) a permselective elastomeric separating layer applied to the membrane.

Suitable fillers are inorganic materials, which preferably have an average particle diameter of 0.05-0.5 μ , particularly preferably 0.2-0.4 μ (determination with the aid of electron microscopy counting methods). Suitable materials for this are titanium dioxide, zirconium dioxide, carbon black, iron oxide, aluminium oxide, SiO₂, gypsum, barium sulphate, zinc oxide, zinc sulphide, talc (magnesium silicate), aluminosilicates, such as kaolinite, "China clay" or mica, calcium carbonate, such as calcite, dolomite, chalk or diatomaceous earth, and zeolites of natural or synthetic origin. Many of the substances mentioned are commercial products from various manufacturers and are equally suitable if they lie within the suitable range of particle diameters and the specific surface area. The pigments can be treated with a dispersing agent in a manner familiar to the expert before their use according to the invention.

Titanium dioxide or a mixture of fillers in which titanium dioxide makes up at least 50% by weight of the mixture is preferably employed. It may be advantageous to employ organically modified titanium dioxide for reasons

of better compatibility with the polymer matrix.

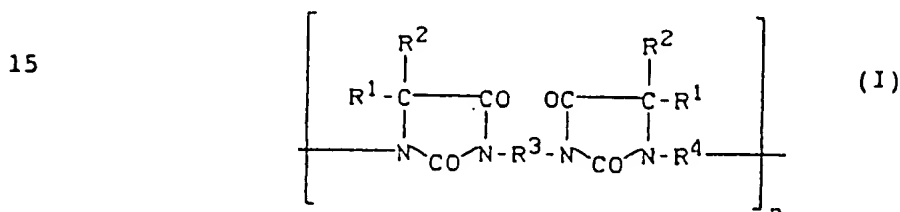
The preferred content of the filler in the total weight of the membrane is 70-90% by weight; the preferred specific surface area is 5-15 m²/g.

5 Film-forming thermoplastic polymers which, with the stated amounts of the fillers mentioned, give a microporous membrane which can be used according to the invention are polycondensates, such as polyamides, polyimides, polyamide imides, polyhydantoins, polymers
10 with aromatic heterocyclic compounds, polyparabanic acids or cyclic polyureas, polysulphones, polyether ketones and polyacrylonitriles and acrylonitrile copolymers, which can optionally carry cationic or anionic groups. Such polymers are known (inter alia DE-OS (German Published
15 Specification) 2,642,979, DE-OS (German Published Specification) 2,554,922, DE-OS (German Published Specification) 1,494,433, DE-OS (German Published Specification) 1,570,552, DE-OS (German Published Specification) 1,720,744, DE-OS (German Published
20 Specification) 1,770,146, DE-OS (German Published Specification) 2,003,398, EP 4,287 and EP 8,895); from these polymers, all of which, together with the fillers, form microporous membranes having pore diameters in the range from 0.001 to 10.0 μ m, the expert can select the
25 one which is chemically the most suitable for use on certain substance mixtures to be treated by pervaporation.

These polymers should have a softening point above 120°C, preferably above 150°C, in order to have an
30 adequate margin for the process temperature of the

pervaporation and gas separation. These requirements are preferably met by a polymer from the group comprising polyhydantoins, polysulphones, polyether ketones, polyamides, polyimides, polyamide imides and polyparabanic acids. Such polymers particularly preferably contain aromatic groups in the polymer chain, for example polyamides of phenylenediamine and isophthalic acid, polyamides of hexamethylenediamine and an aromatic dicarboxylic acid, such as terephthalic acid or isophthalic acid, polyimides of trimellitic acid or pyromellitic acid and an aromatic diamine or diisocyanate, or polysulphones of bisphenol A and bis(p-chlorophenyl) sulphone.

Polymers which have proved to be especially suitable are polyhydantoins of the following formula



wherein

R^1 and R^2 independently of one another denote C_1 - C_8 -alkyl and

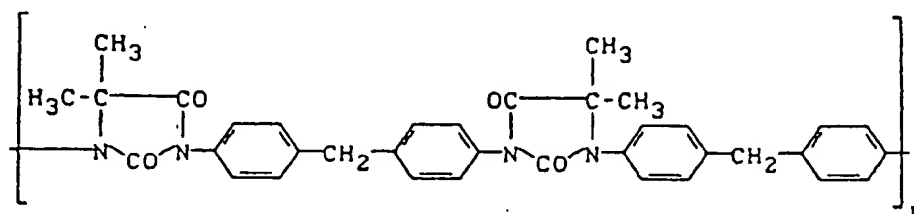
R^3 and R^4 independently of one another denote C_2 - C_8 -alkylene, C_6 - C_{12} -arylene, $-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-$ or $-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-$.

C_1 - C_8 -alkyl is, for example, methyl, ethyl, propyl, butyl, hexyl or octyl, and branched isomers thereof; C_2 - C_8 -alkylene is, for example, ethylene, propylene, butylene, hexylene or octylene, and branched

isomers thereof. C_6 - C_{12} -arylene is, for example, phenylene, biphenylene or naphthylene, preferably phenylene. At least one of the radicals R^3 and R^4 is furthermore preferably arylene.

5 The values for the index n can vary within wide limits and are 2-200, preferably 2-150.

The diphenylmethane-polyhydantoin of the following formula may be referred to as an example:



(II).

10 Whereas semipermeable membranes of the thermoplastics mentioned already shrink irreversibly, in a manner known to the expert, when they dry slightly, the membranes to be employed according to the invention which
15 are enriched with inorganic fillers exhibit no deterioration in their properties here and thus retain their pronounced surface porosity.

20 The composite membrane according to the invention furthermore consists of a permselective elastomeric separating layer applied to the membrane according to i). For this, these elastomeric polymers are applied to the microporous membrane by means of a conventional casting technique. Examples of elastomeric polymers are polybutadiene, polyisoprene, polychloroprene, poly(butadiene-co-styrene), poly(dimethylsiloxane), butadiene-acrylonitrile

copolymers, polyether urethane and/or polyester urethane and polyurethane-polyureas. Some of these polymers, such as polybutadiene and poly(butadiene-co-styrene), only achieve their elastomeric properties after crosslinking (vulcanization) by heat or caused by activating radiation. Examples of solvents for the application of these polymers are:

Toluene, cyclohexane, tetrahydrofuran, acetone, methanol, methyl ethyl ketone, ethyl acetate, dimethylformamide, alkanes and water, if the elastomers are employed in the form of their aqueous dispersions. Mixtures of these solvents can also often advantageously be used.

The casting solutions contain the elastomeric polymers in a concentration of 5 to 50% by weight, preferably 10 to 25% by weight, based on the total casting solution.

The mechanical stability of the composite membranes according to the invention can furthermore advantageously be increased by a procedure in which the microporous membrane according to i) is first applied to a support layer of coarse porosity made of a non-woven fabric or a woven fabric, before the separating layer according to ii) is applied to i). Materials for this support layer of coarse porosity are, inter alia, polyethylene, polypropylene, polyamide, polyester, polyphenylene sulphide or glass fibres in the form of non-woven fabrics or woven fabrics.

The invention furthermore relates to a process for the preparation of the abovementioned composite

membranes, which is characterized in that

- 5 a) a filler having a specific surface area of 5-200 m²/g is dispersed in an amount of 60-90% by weight, based on the weight of the polymer and of the filler, into the solution of a film-forming polymer, a homogeneous casting solution having a viscosity of 500-15,000 cp being formed,
- 10 b) this solution is processed to give a membrane in the form of a film, a tube, a hose or a hollow fibre, the solvent being removed by precipitation coagulation, and
- 15 c) a permselective elastomeric separating layer is applied to the membrane in the form of a solution of the elastomer, with subsequent removal of the solvent by evaporation, and if appropriate the final state of the elastomer is produced by crosslinking (radiation or heat).

The precipitation coagulation can be combined with the additional evaporation of the solvent.

- 20 Sutable solvents here are: dimethylformamide (DMF), N-methyl-pyrrolidone (NMP), dimethyl sulphoxide (DMSO), dimethylacetamide, dioxolane, dioxane, acetone, methyl ethyl ketone or cellosolve, preferably DMF and NMP, particularly preferably DMF. To achieve the viscosity mentioned, the polymer is in general contained in the solution in a concentration of 6 - 10% by weight, based on the total casting solution. Filler is dispersed into such solutions with the aid of a rapid-rotating stirrer (dissolver). Such dispersions can additionally also
- 25 contain about 1-10% by weight of CaCl₂ or LiCl, based on
- 30

the total weight of the dispersion, as pore-forming components. Such dispersions as the casting solution are degassed by being left to stand or applying a weak vacuum and are then applied in layer thicknesses of 50-400 μ , preferably 80-150 μ , to a carrier substrate with the aid of a doctor blade. The solvent is then removed by evaporation or, preferably, by dipping into a coagulation bath, for example into pure water. After a residence time of, for example, 2 minutes, the microporous membrane containing fillers can be removed from the coagulation bath and dried with hot air.

The carrier substrate employed for the application of the casting solution can be one which merely serves to prepare the microporous membrane according to i) containing fillers, and is therefore peeled off again from i) after the coagulation operation. For this, the carrier substrate must be smooth and is, for example, glass, polyethylene terephthalate film or a siliconized carrier material. However, if the composite membrane according to the invention of i) and ii) is to be provided with a support material for improving the mechanical stability, materials which are permeable to liquid are used as the carrier substrate, such as non-woven fabric or woven fabric, to which the microporous membrane i) containing filler exhibits good adhesion. Examples of suitable materials for such a support layer of coarse porosity are, as already described above, polyethylene, polypropylene, polyester, polyamide, polyphenylene sulphide or glass fibres in the form of non-woven fabrics or woven fabrics. The simultaneous use

of such a support layer is preferred for the preparation of the composite membranes according to the invention.

Before the membrane is dipped into a coagulation bath, 1-30% by weight of the solvent used can be evaporated at a temperature of 40-100°C.

It is furthermore known that, to increase the surface area of membranes, as well as being used in the form of films, the preparation of which has just been described, these can also be used in the form of tubes, hoses or hollow fibres. To achieve maximum membrane surface areas with the minimum possible apparatus volumes, these can be arranged and used in specific separating units (modules). Such tubes, hoses or hollow fibres can be prepared, for example, using a concentric two-component nozzle and forcing the above-described casting solution containing filler through the outer annular gap, whereas a coagulating agent, such as water, and in addition air or an inert gas are forced through the central nozzle opening, the casting solution issuing from the nozzle also entering into a coagulation bath, such as water; coagulation is in this way performed from the inside and from the outside.

After removal of the solvent by evaporation or by coagulation and drying, a permselective elastomeric separating layer is applied to the microporous membrane i) containing filler by the casting technique. In this procedure, for practical reasons it is very advantageous that the microporous membranes i) containing filler can be stored, handled and further processed in the dry state without changing their pore structure.

The thickness of this separating layer is 0.5-500 μ , preferably 5-50 μ .

5 The composite membranes according to the invention are outstandingly suitable for use in processes for pervaporation and gas separation.

The invention thus furthermore relates to such processes for pervaporation and gas separation, which are characterized in that a composite membrane of the type described above is employed.

10 An apparatus such as is described in DE-AS (German Published Specification) 2,627,629 has been used for carrying out the pervaporation. In this, the composite membranes prepared were used in a measurement apparatus which can be screwed together, the upper half
15 of which consisted of a cylindrical chamber having a capacity of 300 ml, into which the mixture to be separated (feed) was introduced. The lower part of the apparatus was an approximately hemispherical cover of low volume with a discharge connector. The composite membrane
20 to be tested was supported on the permeate side by a sintered metal plate; the apparatus was sealed by Teflon sealing rings between the upper part and the membrane and between the sintered plate and lower part of the apparatus which can be screwed together. The charging side of
25 the composite membrane was under the hydrostatic pressure of the feed under atmospheric pressure, and the permeate was continuously sucked off on the permeate side of the membrane. For this, the discharge connector of the
30 apparatus was connected to a vacuum pump by a line via three cold traps connected in series, which were cooled

with a dry ice-acetone mixture. The permeate was condensed virtually completely in the cold traps. The active membrane area was 39.6 cm².

5 Other experiments were carried out with the aid
of a pervaporator module as described in DE-OS (German
Published Specification) 3,441,190. Such a module consists of a plurality of flat components combined in the
10 same way as filter presses or plate heat exchangers, each pervaporator unit consisting of a feed chamber and a permeate chamber separated from this by means of the composite membrane according to the invention, a large number of pervaporator units being connected in parallel to form a module, a condenser constructed in the same way being applied to the module and the module and the
15 condenser being combined to form one component by means of cover plates and tension rods, suitable seals being inserted as intermediate layers and connecting, feed and removal channels being formed at the edge.

20 The composite membranes according to the invention, in particular in their preferred embodiment with a support layer of a non-woven fabric or a woven fabric, are suitable for a large number of such pervaporation tasks. Thus, for example, it is possible to remove organic substances from water with a high separation
25 effect. As organic substances there may be understood here: alcohols, such as methanol, ethanol, propanol, butanol and the like; esters, such as ethyl acetate, methyl acetate, methyl propionate and the like; aldehydes and ketones, such as acetaldehyde, acetone, butanone and
30 the like; aromatic compounds, such as phenol, aniline,

chlorobenzene, toluene, cresol, the isomeric chloro-
toluenes and the like; chlorinated aliphatic hydro-
carbons, such as methylene chloride, chloroform and the
like; and ethers, such as diethyl ether, tetrahydrofuran,
5 dioxane and the like. These organic substances mentioned
as examples are characterized by a water solubility which
is at least low and a vapour pressure which is adequate
for the pervaporation process. Those composite membranes
10 according to the invention in which the microporous
membrane i) containing fillers has been finished with
poly(dimethylsiloxane) as the elastomeric separating
layer ii) have proved to be particularly suitable, for
example, for these separation tasks. The removal of
15 organic substances in a concentration range of 10% down
to 1 ppm is appropriate according to the pervaporation
process. To form the elastomeric separating layer, for
example, poly(dimethylsiloxanes) which contain on the one
hand vinylsilane groups and on the other hand hydrido-
20 silane groups and which undergo a hydrosilylation reac-
tion, as a crosslinking reaction, by means of heat and
under catalysis of a platinum compound are employed.
Crosslinking reactions of poly(siloxane) are also pos-
sible by peroxidic crosslinking of poly(siloxane) con-
25 taining vinyl groups, by photochemical crosslinking of
poly(siloxane) containing acrylate or methacrylate groups
or by condensation of hydroxyl-containing poly(siloxane)
with tri- or tetrafunctional silicon compounds, for
example silicon tetraacetate.

30 Composite membranes according to the invention
which carry on the microporous membrane i) containing

fillers an elastomeric separating layer ii) of cross-linked poly(butadiene) and butadiene-styrene copolymers (random copolymers or block copolymers) or poly(norbornene) or poly(octenamer) or poly(butadiene-co-acrylonitrile) or ethene-propene copolymers, such as, for example, EPDM rubber with ethylidene-norbornene units, are furthermore suitable for this separation task of separation of organic substances, such as have been described above, from water.

The poly(butadienes) can be crosslinked by addition of small amounts (0.1 to 4% by weight) of a free radical crosslinking agent, for example diisopropyl peroxydicarbonate or dibenzoyl peroxide as a free radical crosslinking agent, at elevated temperature (typically 40-80°C), or by sulphur-containing crosslinking reagents. A suitable molecular weight range for such poly(butadienes) is about $M_n = 500,000 - 2,000,000$ g/mol. The build-up of the poly(butadiene-co-styrenes) can be a random distribution of the styrene monomer unit in the poly(butadiene), or in the form of a tri-block copolymer with styrene end blocks and a poly(butadiene) central part. The crosslinking reaction and molecular weights of these butadiene-styrene copolymers are analogous to those of the pure poly(butadienes).

Another task to be achieved with the composite membranes according to the invention by pervaporation is the removal of benzene, toluene, xylene, ethylbenzene, propylbenzene, chlorobenzene, dichlorobenzene, bromobenzene, phenol, aniline and other aromatic substances from aliphatic or cycloaliphatic hydrocarbons. Outstanding

results have been achieved in this separation task if, in the context of the composite membranes according to the invention, the microporous membrane i) containing fillers has been coated with an elastomeric separating layer ii) of elastomeric polyurethanes. Such a microporous membrane coated by elastomeric polyurethanes, such as polyester-urethanes or polyether-urethanes, is similarly outstandingly suitable for carrying out the removal of benzene, toluene, xylene, ethylbenzene, propylbenzene, chlorobenzene, dichlorobenzene, bromobenzene, phenol, aniline or other aromatic substances from water.

The separation factor α , which represents a measure of the selective permeability of the membrane, is in general quoted as a measure of the separating action; it is defined by the following equation:

$$\alpha = \frac{C_{Ap}}{C_{Bp}} \times \frac{C_{Bm}}{C_{Am}}$$

in which

C_{Ap} and C_{Bp} denote the concentrations of substances A and B in the permeate (p) and

C_{Am} and C_{Bm} denote the corresponding concentrations in the mixture (m) to be separated (feed),

wherein

A in each case denotes the component to be removed and

B denotes the other or the remaining components of the mixture.

Because of the fundamental similarity, as

described above, of pervaporation with gas separation in the case where the feed is brought in gaseous form to the membrane, the composite membranes according to the invention are likewise outstandingly suitable for gas separation. To investigate gas separation, in the case of ideally miscible gases it is not necessary to investigate a gas mixture, but it is adequate to test the individual gases in pure form on the membranes.

The separation capacity of such membranes for such gases can then be described by the ratio of the individual gas permeabilities to one another. A membrane is selective for a gas A over a gas B if

$$\frac{P_A}{P_B} > 1$$

wherein P_A and P_B denote the permeabilities of gas A and B.

Example 1: Preparation of a porous support structure, polyhydantoin containing TiO_2

A casting solution consisting of
800.0 g of an 18% strength solution of diphenylmethane-polyhydantoin in N-methylpyrrolidone (NMP);
816.0 g of titanium dioxide (commercial product R-KB[®] from Bayer AG), suspended in the solution with the aid of a dissolver; and

480.0 g of NMP, was prepared, the desired viscosity of 3,850 cP being reached.

The weight ratio of thermoplastic polymer/filler was 15:85.

The casting solution was filtered through a 25 μ m metal sieve with the aid of a pressure filter, degassed in vacuo and applied to a polypropylene non-woven fabric with a wet application of 150 μ m using a doctor blade.
5 The polymer was coagulated in pure water and the finished membrane was dried with hot air.

The following can likewise be used as the carrier non-woven fabrics: polyethylene non-woven fabric, polyester non-woven fabric, polyester woven fabric, poly-
10 phenylene sulphide non-woven fabric or glass fibre woven fabric.

Example 2: Preparation of a porous support structure
polyacrylonitrile containing TiO_2

Analogously to Example 1, a polymer/filler
15 dispersion (15:85) having a viscosity of 4,680 cP was prepared from

400.0 g of Dralon T solution, 14% strength in DMF,
317.3 g of titanium dioxide R-KB 2 and
100.0 g of DMF,

20 and was processed to give a porous carrier structure in the same manner as in Example 1. The carrier non-woven fabrics used were: polypropylene non-woven fabric and polyester non-woven fabric.

Example 3: Preparation of a porous support structure,
25 polyamide containing TiO_2

Analogously to Example 1, a polymer/filler
dispersion (15:85) having a viscosity of 2,260 cP was prepared from

400.0 g of Durethan T 40 solution, 15% strength in DMF,
30 18.0 g of CaCl_2 , powdered,

340.0 g of titanium dioxide R-KB 2 and
50.0 g of DMF

and processed on a polypropylene non-woven fabric to give
a porous carrier structure in the same manner as in
Example 1.

Example 4: Preparation of a porous support structure
polysulphone containing TiO_2

Analogously to Example 1, a polymer/filler
dispersion (15:85) having a viscosity of 3,520 cP was
prepared from

800.0 g of an 18% strength solution of polysulphone (Udel
3500) in N-methylpyrrolidone;

816.0 g of titanium dioxide (commercial product R-KB[®] from
Bayer AG), suspended in the solution with the aid
of a dissolver; and

480.0 g of NMP ,
filtered, degassed and processed on a polyester non-woven
fabric to give a porous carrier structure in the same
manner as in Example 1.

Example 5: Preparation of a composite membrane, poly-
(dimethylsiloxane) as the active separating
layer

The porous support structures described in
Example 1-3 were coated with a 50% strength solution of
a poly(dimethylsiloxane) which can be crosslinked by heat
(commercial product Silopren 2530[®] from Bayer AG) in
toluene in a wet layer thickness of 100 μm . After the
solvent had been evaporated, crosslinking by means of
heat was carried out at 80°C for one hour.

Ex-ample	support structure from Example	Coating material	Dry layer thickness
5	5a	1	Silopren 2530 50 μ m
	5b	2	Silopren 2530 50 μ m
	5c	3	Silopren 2530 50 μ m
	5d	4	Silopren 2530 50 μ m
10	<u>Example 6:</u> Preparation of composite membranes, poly-(butadiene) as the active separating layer		
15	The porous support structure described in Example 1 was coated with poly(butadiene) and poly(butadiene-co-styrene) in toluene solution. The dry layer thickness of the active separating layer was calculated from the solids content of the particular casting solution used and the thickness of the wet application. Some of the elastomers, as the active separating layer, mentioned in the following table were crosslinked by heat treatment of the cast membrane at 80°C for 16 hours, dibenzoyl peroxide in the stated amounts in % by weight having first been added to the particular casting solution as a crosslinking agent.		
20			

Ex- ample	Support structure from Example	Coating material	Cross- linking agent content	Dry layer thickness [μm]
5				
	6a	1	Buna 22 CB	35
	6b	1	Buna 22 CB	0.3 % 35
	6c	1	Buna 22 CB	0.6 % 35
	6d	1	Buna 22 CB	0.9 % 35
10	6e	1	Buna EM 1500	30
	6f	1	Solpren 1205	30
	6g	1	Solpren BL 6533	30
	6h	4	Buna 22 CB	0.9 % 35

15 Buna 22 CB is a poly(butadiene) having a cis-content of 98% and a number-average molecular weight of $M_n = 600,000 - 700,000$. Buna EM 1500 is a random copolymer of 77% by weight of butadiene and 23% of styrene. Solpren 1205, in contrast, is an SBS tri-block copolymer containing a total of 25% by weight of styrene and 75% of butadiene, and Solpren BL 6533 is a block copolymer containing 40% by weight of styrene.

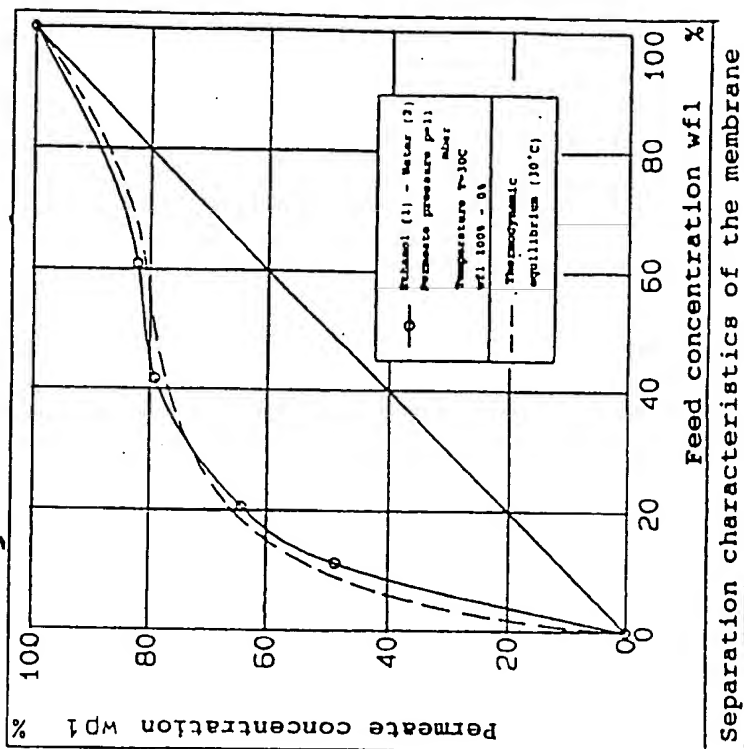
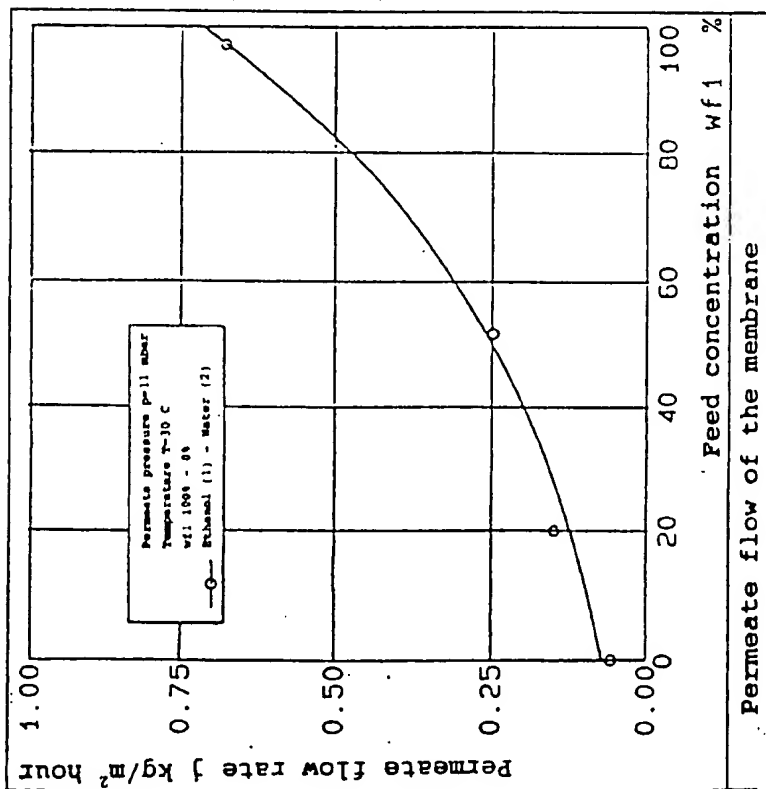
20 Example 7: Use of the composite membranes for removing ethanol from water by pervaporation

25 The pervaporation experiments were carried out in an apparatus such as is described in DE-AS (German Published Specification) 2,627,629, using a mixture of 10% of ethanol and 90% of water; the experiments in each case lasted 4 hours at room temperature and the composition of the permeate was determined by refractometry.

	Composite membrane according to	Permeate pressure	Permeate flow rate g/m ² . h	Concentration of EtOH in the permeate	Separation factor α_{EtOH}
5	Example 5a	3.4 mbar	250	25 %	3.0
	Example 5b	3.5 mbar	184	28 %	3.5
	Example 5c	3.0 mbar	315	26 %	3.1
	Example 5d	0.2 mbar	414	16 %	1.8
10	Example 6a	6.6 mbar	569	19 %	2.2

Example 8:

15 The membrane described in Example 5a was tested with the aid of a pervaporator module, such as is described, for example, in DE-OS (German Published Specification) 3,441,190, by feed solutions of various compositions flowing over it. The experimental conditions and results are shown in Figures 1 and 2.



Figures 1 and 2 (on Example 8): Permeation characteristics and separation action of the membrane according to Example 4a, in Figure 2 the thermodynamic vaporization equilibrium is plotted as a broken line as a comparison for the separation capacity of the membrane.

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Example 9: Use of the composite membranes for the removal of phenol from water by pervaporation

The pervaporation experiments were carried out analogously to Example 7 using different contents of phenol in the feed solution.

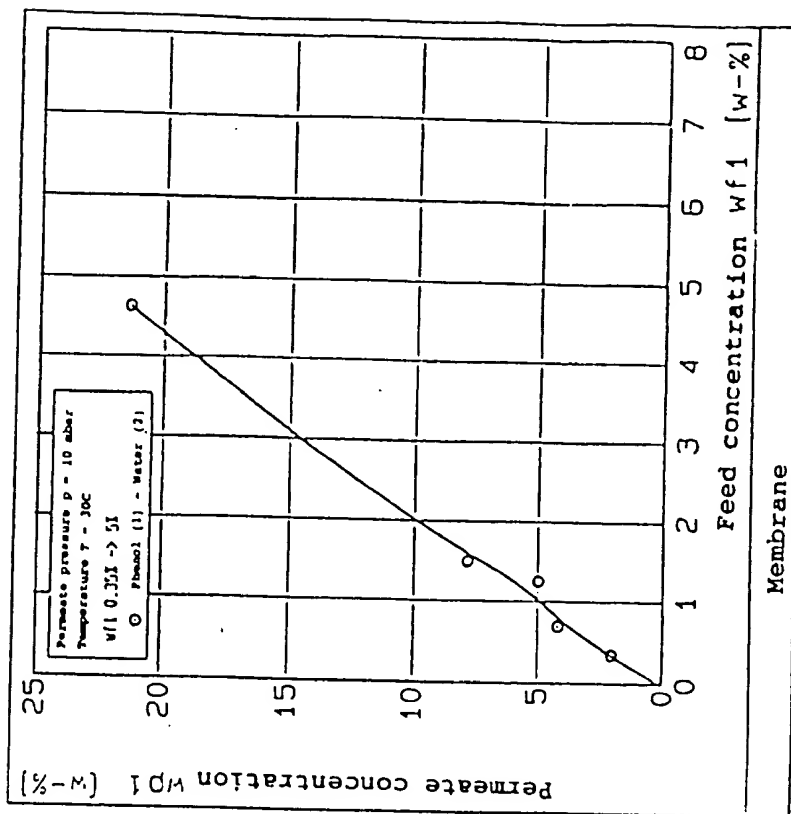
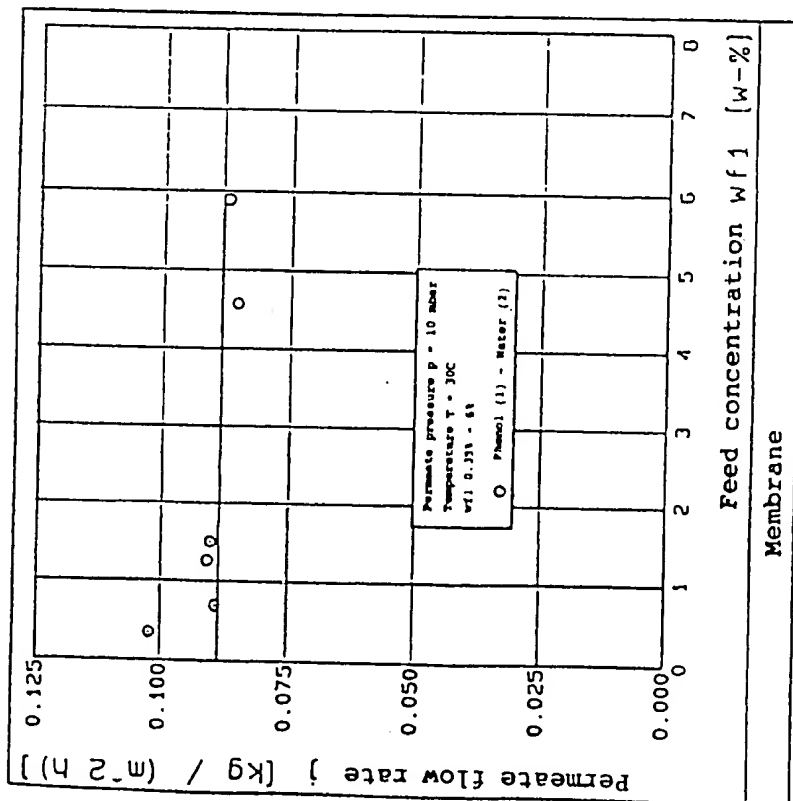
Composite membrane according to	Feed concen- tration of phenol	Permeate pressure	Permeate flow rate g/m ² . h	Concen- tration of phenol in the permeate	Separation factor α_{phenol}
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Example 5a	0.1 %	0.2 mbar	58	0.7 %	6.7
Example 5a	1.0 %	0.3 mbar	37	>10 %*	-
Example 5a	5.0 %	6.0 mbar	58	>10 %*	-
Example 6a	0.5 %	6.8 mbar	179	1.75 %	3.5

* Phase separation occurred in the permeate, so that after the saturation concentration of 10% had been exceeded, the phenol content could no longer be determined by refractometry.

Example 10:

The properties of the membrane according to Example 5a were tested in the same way as in Example 7 with a pervaporator module, by feed solutions (phenol-water) of various compositions flowing over it. The experimental conditions and results are shown in Figures 3 and 4.



Figures 3 and 4: Permeation characteristics and separation action of the membrane according to Example 5a for the removal of phenol from water by pervaporation.

Example 11: Use of composite membranes for the removal of acetone from water by pervaporation (20% by weight of acetone in the feed)

5 The pervaporation experiments were carried out analogously to Example 7.

	Composite membrane according to	Permeate pressure	Permeate flow rate g/m ² . h	Concentration of acetone in the permeate	Separation factor α_{acetone}
10	Example 5d	16 mbar	378	32 %	1.9
	Example 5a	16 mbar	110	85 %	23
	Example 6a	16 mbar	318	45 %	3.3
	Example 6b	15 mbar	181	86 %	24
15	Example 6c	16 mbar	156	86 %	24
	Example 6d	15 mbar	162	85 %	22
	Example 6e	16 mbar	30	48 %	3.7
	Example 6f	18 mbar	73	80 %	16
20	Example 6g	16 mbar	47	62 %	6.5

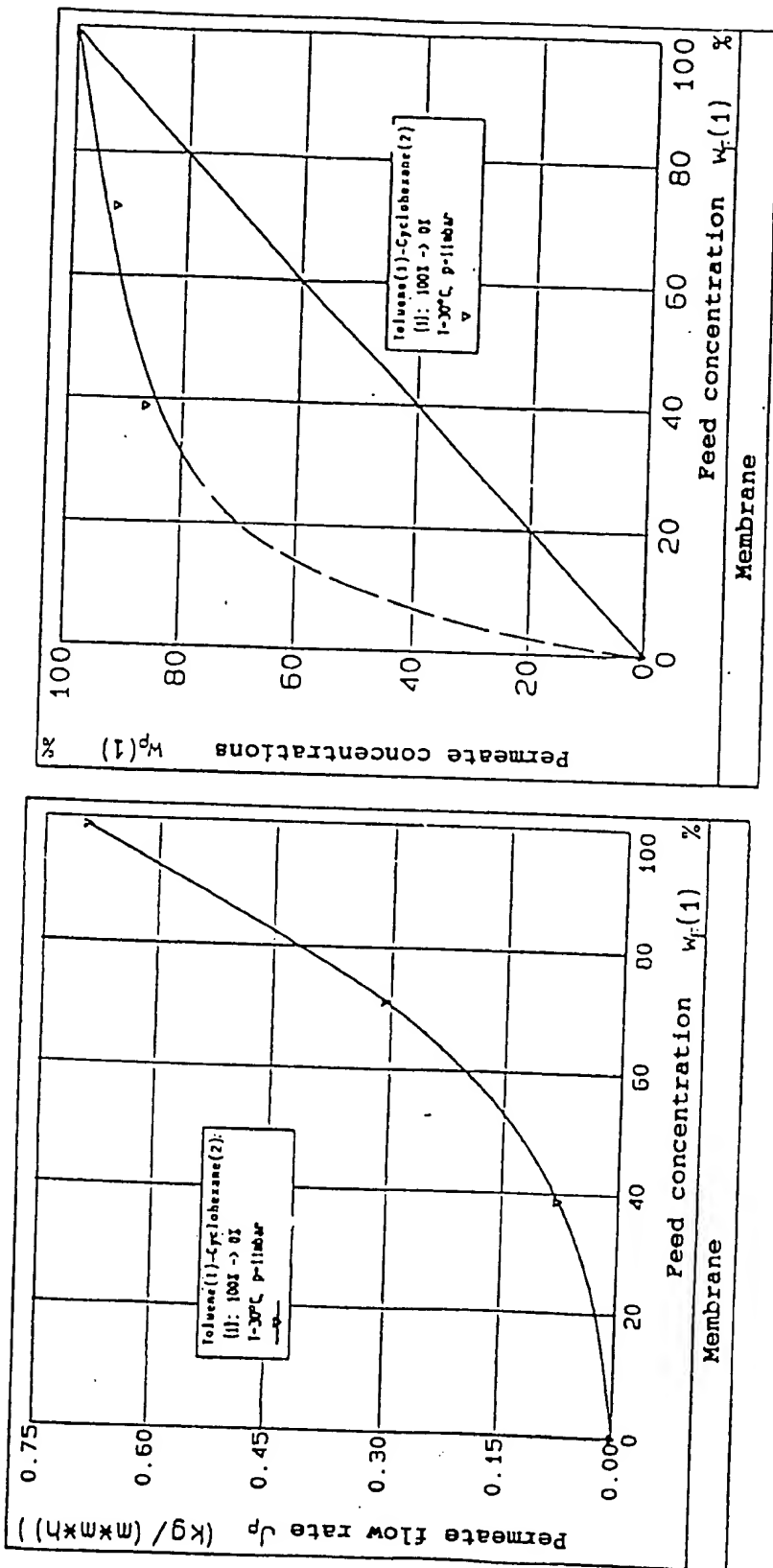
Example 12: Preparation of polyurethane pervaporation membranes for the removal of aromatics from aliphatics

25 The porous membrane matrix obtained according to Example 1 was coated with a polyurethane. For this, 100.0 g of polybutanediol adipate, average molecular weight about 2,250 g.mol⁻¹, 51.7 g of methylene di(phenyl isocyanate) (MDI) and 15 g of butane-1,4-diol

were allowed to react with one another in a known manner. A 30% strength solution (weight/volume) of this polyurethane in a mixture of dimethylformamide and butanone (3:2) was filtered through a pressure filter and left to stand until it was free from bubbles. This polyurethane solution was applied to the porous support membrane described in Example 1 with a wet application of 300 μ m. The solvent was removed with the aid of hot air.

Example 13: Use of the composite membrane from Example 12 for the separation of toluene and cyclohexane by pervaporation

The membrane described in Example 12 was tested with the aid of a pervaporator module, such as is described, for example, in DE-OS (German Published Specification) 3,441,190, by feed solutions (toluene-cyclohexane) of various compositions flowing over it. The experimental conditions and results are shown in Figures 5 and 6.



Figures 5 and 6:

Permeation characteristics and separation action of the membrane according to Example 12 for the separation of toluene and cyclohexane by pervaporation at 30°C and a permeate pressure of 11 mbar.

Example 14: Gas permeabilities of a polyurethane composite membrane

5 A composite membrane as described in Example 12 was prepared with the sole difference that the thickness of the wet application was only 100 μm .

A circular membrane of 8 cm diameter was investigated at 23°C for the gas permeabilities of the following gases:

Gas	Permeability P in	$10^{-6} \cdot \text{m}^3$
		$\text{m}^2 \cdot \text{h} \cdot \text{bar}$
10 Helium	499	
Nitrogen	30	
Oxygen	106	
Carbon dioxide	875	
15 Argon	67	
Methane	71	
Butane	133	

20 A surprisingly good separation capacity for oxygen compared with nitrogen can be seen from the values. The selectivity calculated is

$$\frac{P_{\text{O}_2}}{P_{\text{N}_2}} = \frac{106}{30} = 3,5$$

25 Such a separation capacity enables oxygen from the air to be enriched on the permeate side or oxygen to be depleted on the feed side, which allows, if appropriate, isolation of O_2 -depleted nitrogen as an inert gas.

Patent Claims

1. Composite membrane consisting of
 - i) a microporous membrane, containing inorganic fillers, of a film-forming thermoplastic polymer, the fillers having a specific surface area of $5-200 \text{ m}^2/\text{g}$ and representing 60-90% by weight of the total weight of the membrane, and
 - ii) a permselective elastomeric separating layer applied to the membrane.
2. Composite membrane according to Claim 1, characterized in that the film-forming thermoplastic polymer is chosen from the group comprising polyhydantoins, polyamides, polysulphones, polyether ketones, polyimides, polyamide imides, polyparabanic acids and polyacrylonitriles.
3. Composite membrane according to Claim 2, characterized in that the film-forming thermoplastic polymer contains aromatic monomers and has a softening point of at least 150°C .
4. Composite membrane according to Claim 1, characterized in that the filler is titanium dioxide or a mixture of fillers in which titanium dioxide makes up 50% by weight of the mixture.
5. Composite membrane according to Claim 1, characterized in that polybutadiene, polyisoprene, polychloroprene, poly(butadiene-co-acrylonitrile), an EPDM rubber, poly(butadiene-co-styrene), poly(dimethylsiloxane), polyether urethane or polyester urethane is used as the elastomer for the separating layer.
6. Composite membrane according to Claim 1,

characterized in that the microporous membrane according to i) is first applied to a support layer of coarse porosity made of a non-woven fabric or a woven fabric, before the separating layer according to ii) is applied to i).

7. Composite membrane according to Claim 6, characterized in that polyethylene, polypropylene, polyester, polyamide, polyphenylene sulphide or glass fibre in the form of non-woven fabrics or woven fabrics is employed as the material for the support layer of coarse porosity.

8. Process for the preparation of a composite membrane according to Claim 1, characterized in that

- a) a filler having a specific surface area of 5-200 m²/g is dispersed in an amount of 60-90% by weight, based on the weight of the polymer and of the filler, into the solution of a film-forming polymer, a homogeneous casting solution having a viscosity of 500-15,000 cp being formed,
- b) this solution is processed to give a membrane in the form of a film, a tube, a hose or a hollow fibre, the solvent being removed by evaporation or precipitation coagulation, and
- c) a permselective elastomeric separating layer is applied to the membrane in the form of a solution of the elastomer, with subsequent removal of the solvent by evaporation.

9. Process for pervaporation and gas separation, characterized in that a composite membrane consisting of

- i) a microporous membrane, containing inorganic fillers, of a film-forming thermoplastic polymer, the fillers having a specific surface area of 5-200 m²/g and

- amounting to 60-90% by weight of the total weight of the membrane, and
- ii) a permselective elastomeric separating layer applied to the membrane is employed.

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